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(54) STEEL SHEET COMPOUNDED WITH RESIN

(57)Abstract:

PURPOSE: To provide the above steel sheet compounded with a resin having stabilized high adhesive strength without generating resin peeling at the time of various molding processing.

CONSTITUTION: In the steel sheet compounded with a resin possessing an iron-zinc alloy layer which is heated continuously and alloying-treated after both surface layers of the steel sheet is plated with molten zinc and constituted of at least two steel sheets and an intermediate layer of a viscoelastic substance, a coupling agent treatment is performed on the surface of the iron-zinc alloy layer and a collapsing rate of the surface of the steel sheet is processed within a range of 10-80%. At least one or two kinds of silane coupling agent, titanate coupling agent, aluminum coupling agent and zircoaluminate coupling agent are preferable as the coupling agent and a quantity of a coating film of 0.5-100mg/m² of the coupling agent after drying should be preferable.

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CLAIMS

[Claim(s)]

[Claim 1] In the resin compound-die steel plate which has the iron-zinc alloy layer by which was heated continuously and alloying processing was carried out after hot dip zincing was carried out to both the surface layers of a steel plate, and consists of these two or more steel plates and a viscoelastic-substance interlayer The resin compound-die steel plate excellent in the bond strength characterized by performing coupling agent processing to this iron-zinc alloy layer front face, and being processed on the range whose rate of crushing on this front face of a steel plate is 10 - 80%.

[Claim 2] The resin compound-die steel plate according to claim 1 whose coupling agent is one sort of a silane coupling agent, a titanate system coupling agent, an aluminate coupling agent, and a zircoaluminate system coupling agent, or two sorts or more.

[Claim 3] The resin compound-die steel plate according to claim 1 whose amount of coats after desiccation of a coupling agent is 0.5 - 100 mg/m².

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the resin laminated damping steel sheet in which was applied to the resin compound-die steel plate, and was more excellent in corrosion resistance to operating environment conditions at the detail, and especially the bond strength that influences press-forming nature again was excellent.

[0002]

[Description of the Prior Art] In recent years, the demand of silence nature and silence has increased in various kinds of fields. In the goods field which uses prime movers, such as an automobile and a home-use-electronics product, especially, or the field with the need of controlling the vibration and the noise from the outside effectively like the building-materials application used for a building, application of a useful laminated damping steel sheet is positively advanced to absorption of this vibration and noise energy.

[0003] A steel plate, various plating steel plates, a stainless steel plate, an aluminum plate, a titanium plate, and the so-called restricted type which used the synthetic-resin plate etc. for epidermis material further, and put viscoelasticity macromolecule resin between these two epidermis plates of composite (high-damping material) are applied to this.

[0004] When used for a structural member, the reinforcement of a composite-steel plate is required, and it is common that a steel plate is used as an epidermis plate. Furthermore, when the corrosion resistance under an operating environment is required, the surface treated steel sheet represented by various plating steel plates is used. A hot-dip zinc-coated carbon steel sheet with much [in order to secure corrosion resistance especially] plating coating weight is adopted, and in order to secure the paintwork on the front face of a steel plate, the steel plate with which alloying processing was performed so that JP,54-2911,B might see is adopted in many cases. Moreover, as an approach of performing alloying processing, continuation heat-treatment which is looked at by JP,35-15073,B is performed widely.

[0005] However, in the resin compound-die steel plate using the steel plate which performed such alloying processing, the bond strength of the viscoelasticity intermediate product and steel plate which were put between steel plates produced exfoliation at the time of fabrication depending on the case rather than was enough, and there was a fault which brings about the fatal defect referred to as being unable to perform fabrication well.

[0006] This invention cancels the fault of the above-mentioned conventional technique, and it aims at offering stably the resin compound-die steel plate which has the outstanding bond strength whose shaping is attained by low cost in various configurations in the resin compound-die steel plate using the steel plate which performed alloying processing, without producing resin exfoliation at the time of fabrication.

[0007]

[Means for Solving the Problem] Then, as a result of this invention person's etc. investigating the above-mentioned cause in a detail, the following things became clear. That is, first, since the adhesion at the

time of a laminated damping steel sheet lamination was imperfect, it became clear that the bond strength of resin and a steel plate became low. Furthermore, when it investigates in a detail, it is detailed in the front face of the plating steel plate which carried out alloying processing, and much irregularity is shown in it, and when laminated in a compound-die steel plate, since the viscosity of resin is high, it cannot follow in footsteps of irregularity on the front face of a steel plate enough, and cannot get used to it. Consequently, the true touch area (area which a steel plate front face and resin contact and contributes to adhesion) on a viscoelasticity intermediate product (macromolecule resin) and the front face of a steel plate decreased, and it became clear that the bond strength which can be equal to fabrication was not obtained.

[0008] As the cure, even if it was the case that the viscosity of viscoelasticity macromolecule resin was high, at the lamination process, it is giving the surface roughness to which resin's can follow in footsteps of irregularity of an epidermis steel plate front face, and it became clear that the outstanding bond strength is obtained. Furthermore, it became clear by making resin and a steel plate react to the steel plate (for it to react) front face in contact with macromolecule resin according to a steel plate / resin interface by performing coupling agent processing for the improvement in bonding strength with resin and a steel plate to have been attained. This invention is made here based on the above knowledge.

[0009] Namely, after hot dip zincing of this invention is carried out to both the surface layers of a steel plate, it has the iron-zinc alloy layer by which was heated continuously and alloying processing was carried out, and sets it to the resin compound-die steel plate which consists of these two or more steel plates and a viscoelastic-substance interlayer. Let the resin compound-die steel plate excellent in the bond strength characterized by performing coupling agent processing to this iron-zinc alloy layer front face, and being processed on the range whose rate of crushing on this front face of a steel plate is 10 - 80% be a summary.

[0010] This invention is explained further in full detail below.

[Function]

[0011] Although especially the thickness of the viscoelasticity intermediate product (macromolecule resin) layer used for the resin compound-die steel plate in this invention is not restricted, the range of 10-300 micrometers is desirable, and when it desires much more improvement in the vibration-deadening engine performance, the range of 30-80 micrometers is preferably good. Since the effectiveness that resin film thickness changes and carries out stripping of the vibration-deadening engine performance of resin, i.e., the vibrational energy from the outside, to heat energy in 10 micrometers or less declines rapidly and it becomes impossible to demonstrate the property of laminated damping steel sheet original, it is not desirable. On the other hand, even if resin film thickness exceeds 300 micrometers, although there is no fall of the vibration-deadening engine performance itself, the difference of the reinforcement of resin itself and a steel plate on the strength becomes large too much, at the time of processing shaping on laminated damping steel sheet practical use, the amount of gaps of a steel plate edge becomes large, and it becomes disadvantageous.

[0012] In this invention, in the interface of macromolecule resin (viscoelasticity intermediate product) and an epidermis steel plate, in order to raise the contact condition of the resin and the iron-zinc alloy layer which have high viscosity at the time of a lamination and to secure a true touch area, the front face where the irregularity of alloying processing material is intense is processed by the approach of rolling and others, and the rate of crushing on the front face of a steel plate is managed to 10 - 80%. By this, by adjusting the center line average of roughness height (Ra) to the range of 0.3-2.0 micrometers, the flattery of resin with high viscosity in the irregularity on the front face of a steel plate will be attained at the time of a lamination, not only the anchor effect by the irregularity on the front face of a steel plate but a true touch area will increase, and high bond strength will be obtained.

[0013] The rate of crushing on the front face of a steel plate cannot reduce irregularity on the front face of a steel plate at 10% or less, and since resin with high viscosity cannot follow in footsteps of surface irregularity, the improvement effect of contact reinforcement is not accepted. Since rolling workability becomes high, a crack occurs in a plating layer and destruction of the plating layer itself is produced when securing with rolling on the other hand in order to secure the rate of crushing 80% or more is

considered, bond strength will fall conversely. Therefore, what is necessary is just to manage the surface rate of crushing in 10 - 80% of range.

[0014] In addition, in order to make the number of the functional group of a coupling agent, and the functional groups of resin which contributes to adhesion increase, it is necessary to make high the true touch area of a steel plate front face and resin. For that purpose, since a touch area becomes small in a steel plate front face in respect of [concavo-convex / which is not almost] smooth, the managed concave convex is desirable. Therefore, it is desirable to manage in the range whose Ra specified by the center line average of roughness height is 0.3-2.0 micrometers. The granularity of the front face of an alloying processing as is 2.0-4 micrometers, and on the big front face of such granularity, a true touch area also falls at the same time an anchor effect is not demonstrated, since resin cannot follow in footsteps of irregularity, and bond strength does not become high. Especially this phenomenon is remarkable when the viscosity of the resin at the time of a lamination is high. When viscosity in case a steel plate front face and resin contact and react is 100 or more centipoises, specifically, it becomes remarkable. On the other hand, if surface roughness becomes the detailed irregularity of 0.3 micrometers or less, the anchor effect demonstrated because the irregularity on the front face of a steel plate bites in a resin layer will become small, and a true touch area will also become small, the touch area of the steel plate and resin which are contributed to adhesion cannot be secured, and bond strength will not become high.

[0015] Therefore, the rate of crushing on the front face of a steel plate is specified in 10 - 80% of range. Furthermore, it is desirable to adjust surface roughness to the range of 0.3-2.0 micrometers by Ra. In order to acquire this surface situation, the approach of **, such as performing slight rolling (skin pass) usually performed with cold rolled sheet steel, is mentioned. Moreover, what is necessary is just to take the approach of adjusting the rate of an imprint, using the roll which carried out dull processing of the roll for rolling by the usual approaches, such as shot blasting, so that it may become predetermined granularity in order to obtain center line granularity Ra in the predetermined range.

[0016] Especially the thickness of a plating layer is not limited and can be applied to the thing of the range of the amount of superintendent officers used by usually carrying out alloying processing, i.e., the large range of 20 - 80 g/m². Moreover, it is not restricted especially about the board thickness of a steel plate, either. As a viscoelasticity intermediate product used for this invention, various kinds of resin excellent in the vibration-deadening engine performance is usable, for example, the macromolecule resin of various resin systems of **, such as a polyolefine system, a polyester system, acrylic, an acetic-acid vinyl system, a vinyl chloride system, and acrylic, is usable. Moreover, application of the heat-curing mold resin accompanied by crosslinking reaction and thermoplastic mold resin without crosslinking reaction is possible, and it cannot be overemphasized that a resin system is not restricted at all.

[0017] Like ****, the bond strength which whose bonding strength on a resin front face and the front face of a steel plate improved as mentioned above by the rate of crushing and performing coupling processing further by this invention although high contact reinforcement will be obtained if surface roughness is managed further, and was further excellent in the plating steel plate front face in contact with a viscoelasticity intermediate product is obtained.

[0018] That is, when the metal which is the resin and the inorganic material which are an organic material was compounded, control of the interface which a heterogeneous ingredient touches is important, the coupling agent which functions as this point and interface reforming material is very effective, it acted as both binder in the interface which resin and a steel plate touch, and it became clear that bond strength improved.

[0019] Although a coupling agent makes organic and inorganic react, and has the effectiveness which strengthens inorganic and organic association and it is widely used in the coating field, the dyeing field, etc. In this invention, a cup RIKAGU agent acts as both binder in the interface which resin and a steel plate touch. Bond strength is raised and one sort or two sorts or more of use of a silane coupling agent, a titanate system coupling agent, an aluminate coupling agent, and a zircoaluminate system coupling agent is very effective especially.

[0020] A silane coupling agent is a general formula $YSiX_3$ (however, Y is the organic functional group

in which the organic matrix of synthetic resin and association are possible). for example, a vinyl group, an epoxy group, the amino group, an amide group, a sulfhydryl group, etc. are mentioned, and the alkoxy group which X is the radical of the hydrolysis nature combined with the silicon atom, for example, is shown by OR is mentioned. Are expressed, and for example, alkoxy group OR hydrolyzes with external moisture, and the operation function changes to a silanol group. While the generated silanol (OH) YSi 3 carries out a dehydration condensation reaction to the OH radical combined with the front face of a steel plate metallurgy group filler, builds siloxane association and combines with a metal firmly, the organic functional group Y functions as reacting with the organic front face of resin and performing *****.

[0021] The above-mentioned organic functional group Y is selected according to the class of resin mentioned later. For example, if the organic functional group Y is a vinyl group, unsaturated polyester, an acrylic, polyethylene, etc. are suitable for resin, and if the organic functional group Y is an epoxy group, epoxy, urethane, a melamine, thermosetting polyester, denaturation polyethylene, etc. are suitable for resin. Moreover, when the organic functional group Y is an amino group, epoxy, urethane, a melamine, thermosetting polyester, denaturation polyethylene, a polyvinyl chloride, etc. are suitable for resin.

[0022] A zircoaluminate system coupling agent makes a zirconium/aluminum main frames, various organic ligands are combined with this, one of the organic ligands is constituted so that the inorganic part of a molecule may make a canal and a hydrophilic property stability and may be obtained, and other one has an organic functional group. As a functional group which it has in a JIRUKO aluminate coupling agent, they are the amino group, a carboxyl group, a metacryloxy radical, a fatty acid, etc. As a reaction of such a coupling agent, when a reaction with polyester resin/metal plate is considered, for example, it combines with a front face through a metal plate front face, an oxo-radical, or a hydroxyl group, and the ligation reaction of a zirconium and the aluminum element is carried out to the OH radical of polyester in the carboxyl group of zircoaluminate. For this reason, the bond strength of a metal plate and resin improves.

[0023] A titanate system coupling agent is a coupling agent which contained titanium as a central element, for example, has what has (1) isopropoxy group, the thing which has the residue of (2) oxy-acetic acid, and the thing which has the residue of (3) ethylene glycol as a class of hydrophilic group combined with central element titanium.

[0024] An aluminate coupling agent is a coupling agent of the aluminum organic compound which contained aluminum as a central element, for example, has alcoholate [aluminum (OR)₃ and R:saturated hydrocarbon] and chelates [what has in a molecule the part combined with hydrophilic solid-states (-COOH, -OH, etc.), and the parts (alkyl acetoacetic-acid radical etc.) which keep good relations to the organic substance (ARUKO oxy-radical etc.)].

[0025] The coupling agent which is not hydrolyzed also adds acids, such as a small amount of acetic acid, and the coupling agent which becomes possible also has hydrolysis all effective in this invention at coupling agents other than the above.

[0026] Coupling agent processing uses the above-mentioned coupling agent, and after hydrolysis, it paints it so that it may be approaches, such as a roll coater, and the amount of coats after desiccation may become 0.5 - 100 mg/m² on the front face of visco-elastic polymers or the visco-elastic polymers containing a conductive filler (viscoelastic-substance interlayer), and the metal plate to paste up. As for effectiveness, the improvement in adhesion has few amounts of coats after desiccation of a coupling agent in two or less 0.5 mg/m. Moreover, if the amount of coats after desiccation exceeds 100 mg/m², exfoliation will occur from between coupling agent layers, and adhesion will deteriorate. Therefore, it is desirable to make the amount of coats of the coupling agent after spreading / desiccation into 0.5 - 100 mg/m² on a metal plate front face. In addition, although not limited especially about the drying temperature of a coupling agent, 100-180-degree C desiccation is desirable. Moreover, as for a coupling agent and visco-elastic polymers, it is desirable to exceed 180 degrees C and to make it react at less than 250 degrees C.

[0027] Next, the example of this invention is shown.

[0028]

[Example] The continuous casting aluminum-killed-steel plate of 0.8mm of board thickness was used, after carrying out hot-dip-zincing processing, alloying processing (amount of zinc eyes 45 / 45 g/m²) was performed, and the steel plate which adjusted the rate of crushing and surface roughness on the front face of a steel plate was used as the skin steel plate. Furthermore, it is [Table 1] to a steel plate front face.

| 区 分 | 鋼板表面の 潰れ率 (%) | 中心線 表面粗さ Ra(μm) | カップリング剤の 種類 | カップリング剤の 乾燥後の皮膜量 (mg/m ²) | T剥離強度 (kg/25mm) |
|--------|---------------------|-----------------------|-----------------------|---|--------------------|
| 比較例 1 | 50 | 1.0 | シランカップリング剤 | 0.1 | 6.5 |
| 本発明例 1 | | | | 10 | 13.0 |
| " 2 | | | | 80 | 12.5 |
| 比較例 2 | | | | 150 | 7.0 |
| " 3 | | | チタネート系 カップリング剤 | 0.1 | 6.0 |
| 本発明例 3 | | | | 0.5 | 12.0 |
| " 4 | | | | 50 | 13.0 |
| 比較例 4 | | | | 150 | 6.5 |
| " 5 | | | アルミニウム系 カップリング剤 | 0.1 | 6.0 |
| 本発明例 5 | | | | 10 | 13.5 |
| " 6 | | | | 50 | 13.5 |
| 比較例 6 | | | | 150 | 7.0 |
| " 7 | | | ジルコアルミネート系 カップリング剤 | 0.1 | 6.5 |
| 本発明例 7 | | | | 0.5 | 13.5 |
| " 8 | | | | 50 | 14.0 |
| 比較例 8 | | | | 150 | 7.0 |

(注) シランカップリング剤は信越シリコーン社製KBM403を使用した。

チタネート系カップリング剤は味の素(株)社製KR44を使用した。

アルミニウム系カップリング剤は味の素(株)社製AL-Mを使用した。

ジルコアルミネート系カップリング剤は楠本化成(株)製CPGを使用した。

[Table 2]

| 区 分 | 鋼板表面の 潰れ率 (%) | 中心線 表面粗さ Ra(μm) | カップリング剤の 種類 | カップリング剤の 乾燥後の皮膜量 (mg/m ²) | T剥離強度 (kg/25mm) |
|---------|---------------------|-----------------------|----------------------------------|---|--------------------|
| 比較例 9 | 80 | 0.8 | シランカップリング剤 +チタネート系 カップリング剤 | 0.1 | 6.0 |
| 本発明例 9 | | | | 0.5 | 14.0 |
| " 10 | | | | 100 | 14.0 |
| 比較例 10 | | | | 150 | 6.0 |
| 比較例 11 | 0 | 3.0 | チタネート系 カップリング剤 | 50 | 7.5 |
| 本発明例 11 | 10 | 2.0 | | " | 13.0 |
| " 12 | 80 | 0.8 | | " | 12.0 |
| 比較例 12 | 90 | 0.9 | | " | 7.5 |
| " 13 | 0 | 3.0 | アルミニウム系 カップリング剤 | " | 7.0 |
| 本発明例 13 | 80 | 0.8 | | " | 13.0 |
| 比較例 14 | 90 | 0.9 | | " | 7.5 |
| " 15 | 0 | 3.0 | シランカップリング剤 | 0 | 6.0 |
| " 16 | | | | 50 | 6.5 |
| " 17 | | | | 150 | 7.0 |
| " 18 | | | | 50 | 7.0 |

(注) カップリング剤については表1の脚注を参照。

It was alike, and coupling agent processing was performed so that it might be shown.

[0029] That is, after hydrolyzing a coupling agent, as shown in Tables 1 and 2, the coupling agent was applied to the skin steel plate front face by the roll coater, and after desiccation, it applied so that the

thickness after drying visco-elastic polymers on the skin steel plate might be set to 50 micrometers. The average molecular weight 12,000 and the $T_g = -10$ degree C polyester resin which blended the 5 sections (product made from a Japanese polyurethane industry) of koro roots L as a cross linking agent as visco-elastic polymers were used. The compound-die sound deadener was obtained for other skin steel plates which performed the still more nearly same coupling agent processing on it superposition and by carrying out press forming after drying spreading resin. T peel strength of this compound-die sound deadener was evaluated. T peel strength was measured according to JISK6854. The result is written together to Tables 1 and 2.

[0030] The rate of crushing on the front face of a steel plate is suitable, and each example of this invention which performed coupling agent processing shows the outstanding bond strength so that more clearly than Tables 1 and 2.

[0031]

[Effect of the Invention] The lamination of a resin compound-die steel plate which has the stable high bond strength is possible, without producing resin exfoliation in the resin compound-die steel plate which consists of two or more steel plates and a viscoelasticity intermediate product layer at the time of various kinds of fabrication according to this invention, as explained in full detail above.

[Translation done.]